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# Synthesis and Extraction Studies of Some New Anionic Dye Extractors

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A new series of dodecyl derivatives of non-cyclic and cyclic ethers, as the extractors have been synthesized by imination, reduction of imines and cyclization steps, and the structures were identified by FT-IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and mass spectroscopy. The extraction abilities of these ligands with some anionic dyes [4-(2-pyridylazo)-resorcinol monosodium salt monohydrate (NaPAR), and sodium picrate (NaPIC), and potassium picrate (KPIC)] were determined by UV-VIS spectrophotometry using liquid-liquid extraction method. In this study, all of the synthesized ligands were generally showed higher extraction ability for Na-dyes.

**Keywords** diaza crown ether, extraction, imine, lariat ether, sodium and potassium dyes

## INTRODUCTION

Macrocyclic polyethers, which are commonly called crown ethers, have been utilized as neutral extracting reagent.<sup>[1–3]</sup> The complexation of crown ethers with alkali and alkaline earth metal ions has been well documented. Also, these types of ligands have been synthesized to enhance the stability of the cation–ligand complex and better selectivity. Diaza crown ethers are interesting compounds because of complexation ability with an alkali and transition metal cations which structures between crown ethers containing oxygen atoms and cyclams containing nitrogen atoms.<sup>[4–12]</sup> Diaza crown ethers for solvent extraction are highly potent complexing reagents since their affinity is high for cations and hydrophobic properties and they can be optimized with suitable substituents on the nitrogen atoms.<sup>[13–17]</sup>

The determination of complexation constant of organic ligand-metal ion complexes in water can be examined with different methods by following the extraction of metals to the various organic solvents.<sup>[18–22]</sup> Complexation constants can be easily determined by spectrophotometric methods using metal cation containing dye-ligands.<sup>[23–25]</sup>

The extractive-spectrophotometric determination of sodium and potassium ions as ion-pairs using non-cyclic and cyclic ethers as complexing agent and anionic dyes as colored counter ions is used in this study (Figure 1). The effects of the chain length of non-cyclic and cyclic ethers and two different functional groups of anionic dyes, 4-(2-pyridylazo)-resorcinol monosodium salt monohydrate (NaPAR), and sodium picrate (NaPIC), and potassium picrate (KPIC) have been studied.<sup>[24,26,29]</sup>

## RESULTS AND DISCUSSION

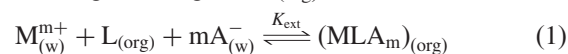
### Synthesis

Starting dialdehyde compounds, **1a–1b** were synthesized according to literature.<sup>[30]</sup> Dodecyl unit containing Schiff bases **2a–2b** have been prepared from **1a–1b** reacting with **1c** in ethanol, respectively. The diamine compounds **3a–3b** have been obtained by reduction of **2a–2b** with NaBH<sub>4</sub> in methanol. The aza crown ethers **4a–4d** have been obtained by the cyclic condensation of the diamines **3a–3b** with bischloride and bistosylate of polyglycols. Accordingly, **3a** has reacted with **1d**, **1e** to afford the aza crown ethers **4a** and **4b**. Compound **3b** has reacted with **1d**, **1e** to afford the aza crown ethers **4c** and **4d**, in presence of Na<sub>2</sub>CO<sub>3</sub> in acetonitrile (Scheme 1).

The characterization of novel lariat ethers (see Experimental Section) were made by using FT-IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and mass spectroscopy.

### Extraction Equilibria

In this paper, we used a common formalism of Equations (1–3).<sup>[27–29]</sup> The equilibrium processes during the extraction between an aqueous solution containing the alkali metal cation, M<sub>(w)</sub><sup>+</sup>, and organic anion, A<sub>(w)</sub><sup>−</sup>, and an organic solution containing diaza ligands L<sub>(org)</sub>, can be written as:



$$K_{ext} = \frac{[MLA_m]_{(org)}}{[M^{m+}]_{(w)}[L]_{(org)}[A^{-}]_{(w)}^m} \quad (2)$$

$$K_{DL} = [MLA]_{(org)} / [M^+]_{(w)} \quad (3)$$

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## STUDIES OF SOME NEW ANIONIC DYE EXTRACTORS

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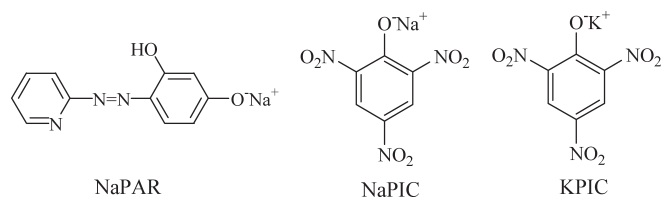


FIG. 1.

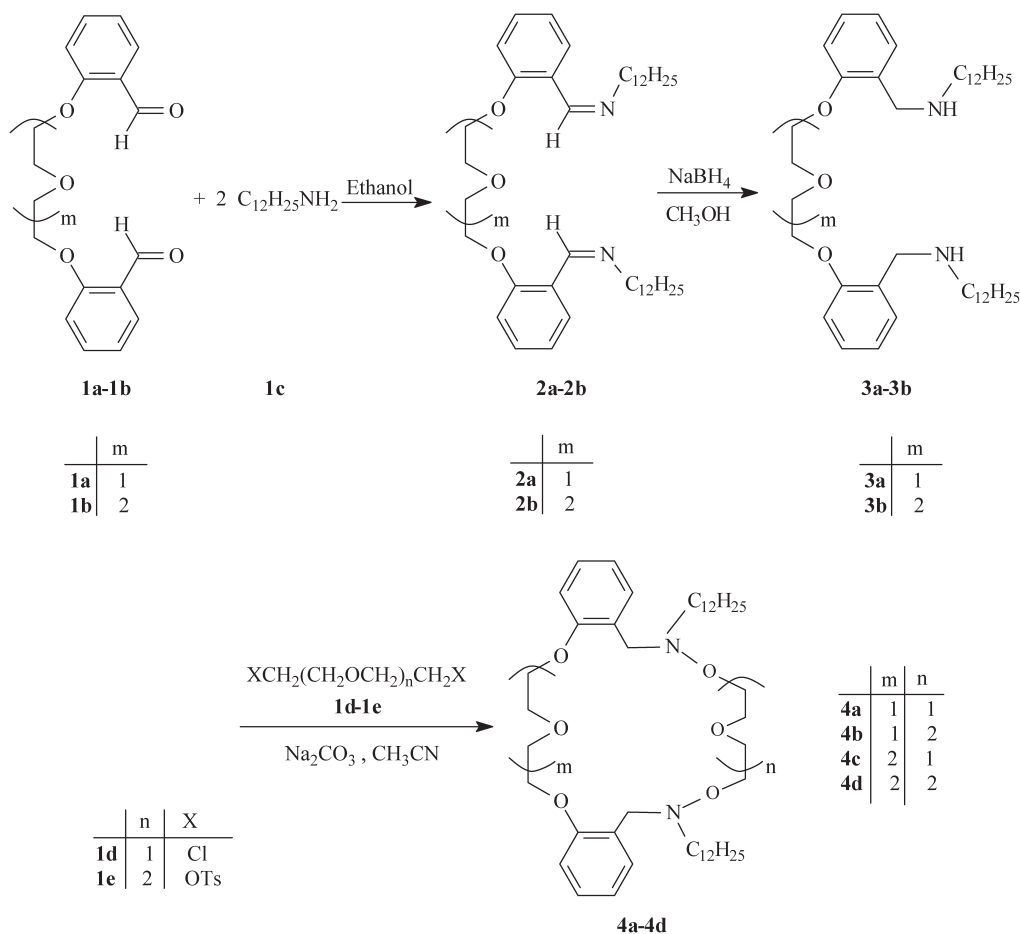
$K_{\text{ext}}$  is extraction equilibrium constant;  $[M^{m+}]$  and  $[MLA_m]$  are the concentration of metal cation in aqueous phase and organic phase, respectively.  $K_{\text{DL}}$  denotes a distribution constant of ligand between organic solvent and water.<sup>[27–29]</sup>

The stability constants of metal complexes of the non-cyclic and cyclic ligands as N-pivot side-armed podands and lariat ethers, i.e., **2a–4d**, are listed in Table 1, as the interactions of these ligands with the alkali metal ions in  $\text{CH}_2\text{Cl}_2$  media. Assuming that formation of 1:1 complexes the alkali metal cations between our ligands extracted at the natural pH of the aqueous metal salt solutions.

The  $\text{Ln } K_{\text{ext}}$  values of the ligands have been decreased with increasing metal ion size (0.095 and 0.133 nm for  $\text{Na}^+$  and  $\text{K}^+$ , respectively,<sup>[31,32]</sup>) i.e.,  $\text{Na}^+ > \text{K}^+$ .

Among the new ligands examined, all podands exhibit low extraction of  $\text{K}^+$ . For  $\text{K}^+$  ion, relatively high extraction percentage are observed with **4d** ligand and amine forms of podands, i.e., **3a** and **3b**.

The  $\text{Na}^+$  ion is wrapped with all of the new ligands better than the larger  $\text{K}^+$  ion. The  $\text{Ln } K_{\text{ext}}$  values well display to extraction selectivity of the ligands for Na-organic salt over for K-organic salt. NaPAR is more strongly complexed with imin forms of the podands in the order of **2b** > **4b** > **2a** > **4d** > **3b** > **4a** > **4c** > **3a**. On the other hand, NaPIC is selectively wrapped around by the amine forms of the podands in sequence of **4d** > **4c** > **3a** > **3b** > **4a** > **2b** > **4b** > **2a** (see Table 1). The lariat crown ethers and podands displayed different extraction characteristics, comparing with an alkali metal cation. For the podands, the complexation constants of sodium metal change by several orders of magnitude depend on the anion of Na-organic salt, namely,  $[\text{PAR}]^- > [\text{PIC}]^-$  and  $[\text{PIC}]^- > [\text{PAR}]^-$  in case of imin and amin forms,



SCH. 1.

TABLE 1  
 $K_{DL}$ , % Ext and  $\text{Ln } K_{\text{ext}}$  values for extraction of **2a**, **2b**, **3a**, **3b**, **4a**, **4b**, **4c**, and **4d** ligands in  $\text{CH}_2\text{Cl}_2$  with NaPAR, NaPIC and KPIC at 25°C

Dyes	Value	Ligands							
		<b>2a</b>	<b>2b</b>	<b>3a</b>	<b>3b</b>	<b>4a</b>	<b>4b</b>	<b>4c</b>	<b>4d</b>
NaPAR	$K_{DL}$	10.09	35.80	1.69	4.11	3.67	21.80	3.42	9.37
	% Ext	90.99	97.28	62.88	80.43	78.58	95.61	77.39	90.35
	$\text{Ln } K_{\text{ext}}$	27.38	31.04	22.76	24.93	24.64	29.59	24.46	27.17
NaPIC	$K_{DL}$	0.79	1.32	15.37	7.61	3.18	1.28	15.49	43.53
	% Ext	44.13	56.96	93.89	88.39	76.06	56.13	93.93	97.75
	$\text{Ln } K_{\text{ext}}$	21.18	22.22	28.58	26.59	24.27	22.15	28.60	31.62
KPIC	$K_{DL}$	0.004	1.00	9.52	4.79	2.57	0.72	2.22	19.21
	% Ext	0.37	50.05	90.49	82.72	71.97	41.71	68.91	95.05
	$\text{Ln } K_{\text{ext}}$	14.67	21.64	27.21	25.33	23.74	21.00	23.39	29.22

respectively. This fact can explain the different effect anions exhibit on the complexation of organic sodium salts with the synthesized ligands.<sup>[33]</sup> We have observed that the  $\text{Na}^+$  complexes of podands were generally found more stable than the complex of its macrocyclic analog of coronands. And this shows the strongest hydrogen bonding of the ether oxygen and nitrogen atoms of podands with Na-organic salts compared with the synthesized coronands. Although not always, open-chain ligands form more stable complexes than do the corresponding macrocycles, this phenomenon was observed with the podands as the open-chain ligands in this study. This difference may explain that podands typically exhibit higher overall basicity than the synthesized coronands.<sup>[34,35]</sup> Naturally, this effect of the nitrogens in podands should make coordination bounds stronger in  $\text{Na}^+$  complexation and more strong hydrogen bonding with counter ion. Thus, in the complexation of podands with the Na-organic salts, the hydrogen bonding causes the  $\text{Ln } K_{\text{ext}}$  values to be higher than of the coronands.

On the other hand, the magnitude sequence of complexation effect of both coronands and podands sometimes showed the changing. The differences between alkali metal salt extracting capabilities of **2a**, **2b**, **3a** and **3b** podands and their corresponding model diaza crown ethers, i.e., **4a**, **4b**, **4c**, and **4d**, except for **2a** in case of  $\text{K}^+$  ion, weren't relatively high.

The above assumption is clearly confirmed by the study of the structural and chemical aspects of complexation in metal salt-macrocyclic polyether systems.<sup>[36]</sup>

In general, the  $\text{Ln } K_{\text{ext}}$  values for  $\text{K}^+$  ion complexation are found relatively smaller than  $\text{Na}^+$  ion complexation of the new lariat crown ethers.

Consequently, the  $\text{Ln } K_{\text{ext}}$  values of  $\text{Na}^+$  complexes are found slightly larger than of  $\text{K}^+$  complexes. The results are show that the higher extractability of  $\text{Na}^+$  organic salts is more attributable to the greater  $\text{Ln } K_{\text{ext}}$  value of

$\text{Na}^+$ -complexation than to the relatively lower  $\text{Ln } K_{\text{ext}}$  value of  $\text{K}^+$ -complexation.

## EXPERIMENTAL

All the used chemicals were purchased from Aldrich or Merck unless otherwise cited. FT-IR spectra have taken a KBr pellet with a Perkin Elmer Spectrum spectrometer, model BX-II, high resolution EI mass spectra have been obtained with Agilent 1100 LC/MSD, NMR spectra have been obtained with a Bruker-Spectrospin AvanceDPX-400 Ultra-Shield  $^1\text{H}$ : 400 MHz  $^{13}\text{C}$ : 100 MHz. CPX and TMS was the internal standard. All melting points reported are uncorrected.

Sodium dye, 4-(2-pyridylazo)-resorcinol monosodium salt monohydrate (NaPAR), was commercial products from Aldrich dried over  $\text{P}_2\text{O}_5$  for 48 h at 0.1 torr. Sodium and potassium picrates were prepared by adding an alkali metal hydroxyde solution to an aqueous solution of picric acid; the resulting precipitate of sodium picrate monohydrate and potassium picrate were recrystallized from a water ethanol (1:3) mixture and water, respectively. The picrate salts were dried at 100°C for 24 h. The dichloromethane used was of analytical-reagent grade.

## Extraction Procedure and Determination of Organic Anions

The overall extraction equilibrium constants for the 1:1 complexes of the above diaza crown ethers and podands with sodium and potassium ions, between the organic solvent and water, have been determined at 25°C. They were conducted in  $\text{CH}_2\text{Cl}_2$ -water systems maintaining an identical initial cation concentration in water,  $[\text{M}_0^+]_{\text{w}}$ , and a macrocyclic ligand concentration in the organic phase,  $[\text{L}_0]_{\text{org}}$ , so that in all extractions  $[\text{M}_0^+]_{\text{w}}:[\text{L}_0]_{\text{org}}$  ratios were 1:1. An ion association complex formed between the alkali-crown ether complex ion

and a metal anion was extracted into the  $\text{CH}_2\text{Cl}_2$  organic solvent, and then the metal concentration of the separated aqueous phase was measured with an ultraviolet-visible spectrophotometer.

The extraction measurements were done in 100 mL glass thermostated cell compartment with a mechanical stirrer where a 25 mL solution of an aqueous salt ( $4 \times 10^{-5}$  M) and ligand in  $\text{CH}_2\text{Cl}_2$  organic solvent in appropriate concentration were placed and stirred for 120 min at  $25 \pm 0.1^\circ\text{C}$  and subsequently allowed to stand for 60 min to complete the phase separation. The optimum concentrations of the ligands were determined by extracting the alkali salts with 10 mL of various concentrations of the ligands ( $4 \times 10^{-5}$  M).

After extraction, the  $\text{Na}^+$  and  $\text{K}^+$  concentrations in the aqueous phase were determined using UV-visible (Varian Cary 1E) spectrophotometer. Each value was the average of three subsequent measurements. Complexation and distribution constants summarized in Table 1.

#### General Procedure for the Synthesis of Dodecyl Unit Containing Schiff Bases (2a–2b)

In a typical reaction, 95.00 mmol of dialdehyde compound was dissolved in 150 mL of ethanol under reflux. Then, 191.00 mmol of dodecylamine (1c) was dissolved in 50 mL of ethanol and added to initial solution at reflux temperature in 1 hour it was cooled. Then a part of ethanol was evaporated. The remaining solution was waited for 24 hours at  $0^\circ\text{C}$ . The precipitated product was obtained as a white solid by suction and crystallized from methanol.

#### Synthesis of 1,15-N,N'-Didodecyl-3,4;12,13-dibenzo-5,8,11-trioxa-1,14-pentadecadiene (2a: $\text{C}_{42}\text{H}_{68}\text{N}_2\text{O}_3$ )

1a was used as the dialdehyde compound. Reactions were done as described above. Yield 89%. mp:  $37\text{--}38^\circ\text{C}$  (methanol).

FT-IR ( $\gamma \text{ cm}^{-1}$ , KBr): 2916, 2847 (C-H); 1641 (Ar-C=N-); 1599 (C=C); 1488, 1448 (C-H); 1244, 1137, (C-O-C); 748 (Ar-H).

$^1\text{H NMR}$  ( $\delta$  ppm,  $\text{CDCl}_3/\text{TMS}$ ): 0.8 (6H, t,  $-\text{CH}_3$ ), 1.2 (36H, m,  $-(\text{CH}_2)_9-$ ), 1.6 (4H, m,  $-\text{N}-\text{CH}_2\text{CH}_2-$ ), 3.5 (4H, t,  $-\text{N}-\text{CH}_2-$ ), 3.9 (4H, t, Ar-OCH<sub>2</sub>-), 4.2 (4H, t,  $\text{CH}_2-\text{O}-\text{CH}_2-$ ), 6.8 (2H, d, Ar), 6.9 (2H, m, Ar), 7.3 (2H, m, Ar), 7.9 (2H, dd, Ar), 8.6 (2H, s, C=NH).

$^{13}\text{C NMR}$ :  $\delta$  ppm 14.52, 21.67, 23.09, 27.83, 29.77, 29.93, 30.06, 30.09, 31.49, 32.33, 34.56, 62.55, 68.64, 70.36, 112.87, 121.70, 125.75, 127.82, 131.94, 156.92, 163.2.

#### Synthesis of 1,18-N,N'-Didodecyl-3,4;15,16-dibenzo-5,8,11,14-tetraoxa-1,17-octadecadiene (2b: $\text{C}_{44}\text{H}_{72}\text{N}_2\text{O}_4$ )

1b was used as the dialdehyde compound. Reaction were done as described above. Yield 92%. mp:  $47\text{--}49^\circ\text{C}$  (methanol).

FT-IR ( $\gamma \text{ cm}^{-1}$ , KBr): 2920, 2849 (C-H); 1638 (Ar-C=N-); 1599 (C=C); 1460 (C-H); 1246, 1135, (C-O-C); 751 (Ar-H).

$^1\text{H NMR}$  ( $\text{CDCl}_3/\text{TMS}$ ): 0.8 (6H, t,  $-\text{CH}_3$ ), 1.2 (36H, m,  $-(\text{CH}_2)_9-$ ), 1.6 (4H, m,  $-\text{N}-\text{CH}_2\text{CH}_2-$ ), 3.5 (4H, t,  $-\text{N}-\text{CH}_2-$ ), 3.7 (4H, s,  $\text{CH}_2-\text{O}-\text{CH}_2$ ), 3.9 (4H, t, Ar-OCH<sub>2</sub>-), 4.2 (4H, t,  $-\text{CH}_2-\text{O}-\text{CH}_2-$ ), 6.9 (4H, m, Ar), 7.3 (2H, m, Ar), 7.9 (2H, m, Ar), 8.6 (2H, s, C=NH).

$^{13}\text{C NMR}$ :  $\delta$  ppm 14.52, 23.08, 27.84, 29.76, 29.94, 30.05, 30.09, 31.50, 32.32, 34.11, 62.53, 68.47, 70.20, 71.37, 112.81, 121.58, 125.67, 127.74, 131.92, 156.75, 162.20.

#### General Procedure for the Synthesis of Dodecyl Unit Containing Diamines (3a–3b)

In a typical reduction reaction, 28.00 mmol Schiff base 2a–2b was stirred to dissolve in 200 mL methanol. 158.70 mmol of  $\text{NaBH}_4$  with small portion was added to this solution and stirred for 12 hours. Then the solvent was evaporated under reduced pressure. The obtained solid was dissolved in chloroform and extracted with 50 mL 0.1 M NaOH. The separated organic phase was washed with water and then the dried on  $\text{Na}_2\text{SO}_4$ . The solvent was removed under reduced pressure. The oily product was purified with silica column using hexane/methanol as a solvent. The obtained compound was as a yellow solid at room temperature.

#### Synthesis of N,N'-Didodecyl-1,15-diamino-3,4;12,13-dibenzo-5,8,11-trioxa-pentadecane (3a: $\text{C}_{42}\text{H}_{72}\text{N}_2\text{O}_3$ )

2a was used as Schiff base and reaction were done as described above. Yield 30%.

FT-IR ( $\gamma \text{ cm}^{-1}$ , KBr): 2923, 2853 (C-H); 1600 (C=C); 1491, 1453 (C-H); 1241, 1134, (C-O-C); 751 (Ar-H).

$^1\text{H NMR}$  ( $\text{CDCl}_3/\text{TMS}$ ): 0.8 (6H, t,  $-\text{CH}_3$ ), 1.2 (36H, m,  $-(\text{CH}_2)_9-$ ), 1.5 (4H, m,  $-\text{HN}-\text{CH}_2\text{CH}_2-$ ), 2.5 (4H, m,  $-\text{HN}-\text{CH}_2-$ ), 2.6 (2H, broad,  $-\text{HN}$ ), 3.7 (4H, s, Ar-CH<sub>2</sub>), 3.9 (4H, t, Ar-O-CH<sub>2</sub>-), 4.2 (4H, t,  $-\text{CH}_2-\text{O}-\text{CH}_2-$ ), 6.7 (2H, d, Ar), 6.9 (2H, m, Ar), 7.2 (4H, m, Ar).

$^{13}\text{C NMR}$ :  $\delta$  ppm 14.51, 21.67, 23.09, 27.81, 29.76, 29.99, 30.05, 30.08, 30.35, 32.32, 34.42, 49.41, 49.67, 67.99, 70.42, 111.81, 121.15, 128.63, 128.84, 130.53, 157.23.

#### Synthesis of N,N'-Didodecyl-1,18-diamino-3,4;15,16-dibenzo-5,8,11,14-tetraoxa-octa decane (3b: $\text{C}_{44}\text{H}_{76}\text{N}_2\text{O}_4$ )

2b was used as Schiff base and reaction were done as described above. Yield 30%. mp:  $33\text{--}35^\circ\text{C}$ .

FT-IR ( $\gamma \text{ cm}^{-1}$ , KBr): 2920, 2852 (C-H); 1595 (C=C); 1457 (C-H); 1240, 1124, (C-O-C); 749 (Ar-H).

$^1\text{H NMR}$  ( $\text{CDCl}_3/\text{TMS}$ ): 0.8 (6H, t,  $-\text{CH}_3$ ), 1.2 (36H, m,  $-(\text{CH}_2)_9-$ ), 1.4 (4H, m,  $-\text{HN}-\text{CH}_2\text{CH}_2-$ ), 1.9 (2H, broad,  $-\text{HN}$ ), 2.4 (4H, t,  $-\text{HN}-\text{CH}_2-$ ), 3.6 (4H, s, Ar-CH<sub>2</sub>), 3.7 (4H, s,  $\text{CH}_2-\text{O}-\text{CH}_2-$ ), 3.8 (4H, t, Ar-OCH<sub>2</sub>-), 4.1 (4H, t,  $-\text{CH}_2-\text{O}-\text{CH}_2-$ ), 6.7 (2H, d, Ar), 6.8 (2H, m, Ar), 7.1 (4H, m, Ar).

$^{13}\text{C NMR}$ :  $\delta$  ppm 14.52, 22.01, 23.09, 27.85, 29.76, 30.06, 30.09, 30.61, 32.32, 33.59, 34.63, 49.62, 49.88, 67.87, 70.31, 71.37, 111.78, 121.03, 128.43, 129.33, 130.33, 157.26.

### General Procedure for the Synthesis of Dodecyl Unit Containing Azacrown Ethers (4a–4d)

The typical reaction procedure for the cyclization reaction leading to macrocyclic ethers (4a–4d) is as follows. A mixture of diamines 3a–3b (3.30 mmol), polyethylene glycol dichloride or polyethylene glycol ditosylate 1d–1e (3.30 mmol), 6.60 mmol Na<sub>2</sub>CO<sub>3</sub> and 6.60 mmol NaI was dissolved 80 mL of CH<sub>3</sub>CN. The mixture was heated for 35–40 h at 80–85°C. The solvent was evaporated in vacuo. The obtained solid product was extracted with CHCl<sub>3</sub>/water (2 × 50 mL). The combined organic phases was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated in vacuo. Chromatograph of the crude products (Al<sub>2</sub>O<sub>3</sub>, Merck) with hexane/ethanol gave pure azacrown ethers.

### Synthesis of N,N'-Didodecyl-1,15-diaza-3,4;12,13-dibenzo-5,8,11,18-tetraoxa-cyclo eicosane (4a: C<sub>46</sub>H<sub>78</sub> N<sub>2</sub>O<sub>6</sub>)

Compounds 3a and 1d and other reagents reacted as described above. Yellow oily product. Yield 35%.

FT-IR (γ cm<sup>-1</sup>, KBr): 3161 (C-H); 2923, 2853 (C-H); 1603 (C=C); 1495, 1453 (C-H); 1256 (C-O-C); 1122 (C-N-C); 757 (Ar-H).

<sup>1</sup>H NMR (CDCl<sub>3</sub>/TMS): 0.8 (6H, t, -CH<sub>3</sub>), 1.2 (36H, m, -(CH<sub>2</sub>)<sub>9</sub>-), 1.4 (4H, m, -N-CH<sub>2</sub>CH<sub>2</sub>-), 2.2 (4H, t, -N-CH<sub>2</sub>-), 2.3 (4H, m, -NCH<sub>2</sub>CH<sub>2</sub>O-), 3.1 (4H, s, Ar-CH<sub>2</sub>), 3.9 (12H, m, O-CH<sub>2</sub>-), 6.8 (2H, m, Ar), 6.9 (2H, m, Ar), 7.3 (2H, m, Ar), 7.7 (2H, m, Ar).

<sup>13</sup>C NMR: δ ppm 14.49, 19.15, 27.70, 30.12, 31.05, 31.59, 32.55, 33.85, 34.20, 34.33, 34.36, 47.71, 58.84, 64.28, 70.94, 72.18, 116.17, 122.22, 126.89, 136.55, 138.24, 157.12.

MS: (m/z) M<sup>+</sup>: 722.4 (5%).

### Synthesis of N,N'-Didodecyl-1,15diaza-3,4;12,13-dibenzo-5,8,11,18,21-pentaoxa-cyclo trieicosane (4b: C<sub>48</sub>H<sub>82</sub>N<sub>2</sub>O<sub>7</sub>)

Compounds 3a and 1e and other reagents reacted as described above. Yellow solid product at room temperature. Yield 38.5%.

FT-IR (γ cm<sup>-1</sup>, KBr): 2924, 2854 (C-H); 1601 (C=C); 1493, 1455 (C-H); 1251 (C-O-C); 1123 (C-N-C); 756 (Ar-H).

<sup>1</sup>H NMR (CDCl<sub>3</sub>/TMS): 0.8 (6H, t, -CH<sub>3</sub>), 1.2 (36H, m, -(CH<sub>2</sub>)<sub>9</sub>-), 1.4 (4H, m, -N-CH<sub>2</sub>CH<sub>2</sub>-), 2.4 (4H, t, -N-CH<sub>2</sub>-), 2.7 (4H, m, -NCH<sub>2</sub>CH<sub>2</sub>O-), 3.5 (12H, m, -CH<sub>2</sub>-O-CH<sub>2</sub>- and Ar-CH<sub>2</sub>), 3.9 (4H, m, Ar-O-CH<sub>2</sub>-), 4.1 (4H, m, -CH<sub>2</sub>-O-CH<sub>2</sub>-), 6.8 (4H, m, Ar), 7.1 (2H, m, Ar), 7.3 (2H, m, Ar).

<sup>13</sup>C NMR: δ ppm 14.52, 21.67, 23.08, 27.89, 29.76, 29.92, 30.05, 30.08, 30.89, 32.32, 34.60, 49.53, 49.92, 64.32, 70.40, 70.75, 72.02, 121.24, 121.98, 126.45, 128.85, 139.21, 157.25.

MS: (m/z) M<sup>+</sup>: 767.9 (10%).

### Synthesis of N,N'-Didodecyl-1,18-diaza-3,4;15,16-dibenzo-5,8,11,14,21-pentaoxa-cyclo trieicosane (4c: C<sub>48</sub>H<sub>82</sub>N<sub>2</sub>O<sub>7</sub>)

Compounds 3b and 1d and other reagents reacted as described above. Yellow oily product. Yield 26%.

FT-IR (γ cm<sup>-1</sup>, KBr): 2924, 2854 (C-H); 1601 (C=C); 1493, 1452 (C-H); 1249 (C-O-C); 1120 (C-N-C); 754 (Ar-H).

<sup>1</sup>H NMR (CDCl<sub>3</sub>/TMS): 0.8 (6H, t, -CH<sub>3</sub>), 1.2 (36H, m, -(CH<sub>2</sub>)<sub>9</sub>-), 1.5 (4H, m, -N-CH<sub>2</sub>CH<sub>2</sub>-), 2.2 (4H, t, -N-CH<sub>2</sub>-), 2.4 (4H, m, -NCH<sub>2</sub>CH<sub>2</sub>O-), 3.8 (20H, m, O-CH<sub>2</sub> and Ar-CH<sub>2</sub>-), 6.7 (2H, m, Ar), 6.9 (2H, m, Ar), 7.2 (2H, m, Ar), 7.7 (2H, m, Ar).

<sup>13</sup>C NMR: δ ppm 14.53, 19.17, 27.72, 31.53, 31.89, 32.15, 32.34, 32.55, 34.16, 34.30, 34.38, 48.85, 58.35, 64.27, 71.97, 72.75, 72.96, 116.61, 125.92, 126.35, 134.68, 136.01, 157.22.

MS: (m/z) M<sup>+</sup>: 767.8 (10%).

### Synthesis of N,N'-Didodecyl-1,18-diaza-3,4;15,16-dibenzo-5,8,11,14,21,24-hekzaoksa-cyclohexaeicosane (4d: C<sub>50</sub>H<sub>86</sub>N<sub>2</sub>O<sub>8</sub>)

Compounds 3b and 1e and other reagents reacted as described above. Yellow solid product at room temperature. Yield 23%. mp: 40–42°C.

FT-IR (γ cm<sup>-1</sup>, KBr): 2920, 2851 (C-H); 1599 (C=C); 1491,1450 (C-H); 1239 (C-O-C); 1130 (C-N-C); 752 (Ar-H).

<sup>1</sup>H NMR (CDCl<sub>3</sub>/TMS): 0.8 (6H, t, -CH<sub>3</sub>), 1.2 (36H, m, -(CH<sub>2</sub>)<sub>9</sub>-), 1.4 (4H, m, -N-CH<sub>2</sub>CH<sub>2</sub>-), 2.5 (4H, m, -N-CH<sub>2</sub>-), 2.7 (4H, m, -NCH<sub>2</sub>CH<sub>2</sub>O-), 3.4 (4H, s, Ar-CH<sub>2</sub>-), 3.5 (4H, t, -OCH<sub>2</sub>CH<sub>2</sub>N-), 3.7 (8H, m, CH<sub>2</sub>-O-CH<sub>2</sub>), 3.8 (4H, t, Ar-O-CH<sub>2</sub>-), 4.1 (4H, t, -CH<sub>2</sub>-O-CH<sub>2</sub>-), 6.7 (2H, d, Ar), 6.8 (2H, m, Ar), 7.1 (2H, m, Ar), 7.3 (2H, d, Ar).

<sup>13</sup>C NMR: δ ppm 14.55, 19.21, 27.78, 31.96, 32.49, 34.45, 34.66, 34.74, 34.77, 37.01, 34.65, 47.95, 58.17, 69.55, 71.11, 73.07, 74.50, 74.99, 116.62, 125.65, 131.11, 133.07, 133.62, 156.98.

MS: (m/z) M<sup>+</sup>: 811.9 (100%).

## REFERENCES

1. C.J. Pedersen, Cyclic Polyethers and their Complexes with Metal Salts, *J. Am. Chem. Soc.*, **1967**, 89, 7017–7036.
2. C.J. Pedersen, Crystalline Salt Complexes of Macrocyclic Polyethers, *J. Am. Chem. Soc.*, **1970**, 92, 386–391.
3. C.J. Pedersen, New Macrocyclic Polyethers, *J. Am. Chem. Soc.*, **1970**, 92, 391–394.
4. K.E. Krakowiak, J.S. Bradshaw, and D.J. Zamecka-Krakowiak, Synthesis of Aza-crown Ethers, *Chem. Rev.*, **1989**, 89, 929–972.
5. J.S. Bradshaw, K.E. Krakowiak, and R.M. Izatt, Aza-crown Macrocycles, In *Chemistry of Heterocyclic Compounds*, **1993**, J.Wiley & Sons Inc., New York, Vol. 51.
6. R.M. Izatt, J.S. Bradshaw, S.A. Nielsen, J.D. Lamb, J.J. Christensen, and D. Sen, Thermodynamic and Kinetic Data for Cation-macrocyclic Interaction, *Chem. Rev.*, **1985**, 85, 271–339.
7. R.M. Izatt, K. Pawlak, J.S. Bradshaw, and R.L. Bruening, Thermodynamic and Kinetic Data for Macrocyclic Interactions with Cations and Anions, *Chem. Rev.*, **1991**, 91, 1721–2085.
8. P. Piatek, D.T. Gryko, A. Szumna, and J. Jurczak, A New Strategy for the Synthesis of Pendant Benzodiazacoronands and their use as Components of Chromatographic Stationary Phases, *Tetrahedron*, **2004**, 60, 5769–5776.

9. A. Thaler, B.G. Cox, and H. Schneider, Stability Constants of Aza-oxa-crown Ether Complexes with Silver(I) in Nonaqueous Polar Solvents, *Inorg. Chim. Acta*, **2003**, 351, 123–132.
10. A. Thaler, A. Heidari, B.G. Cox, and H. Schneider, Stability Constants of Copper(I) and Silver(I) Complexes with Open-chain, Macrocyclic and -Bicyclic Aza-ligands in Acetonitrile and Comparison with Results in Dimethylsulfoxide, *Inorg. Chim. Acta*, **1999**, 286, 160–168.
11. H.J. Buschmann, E. Cleve, S. Torkler, and E. Schollmeyer, The Determination of Complex Stabilities with Nearly Insoluble Host Molecules. Complexation of Barium(II) with Substituted Diaza-18-crown-6 Ligands in Aqueous and Methanolic Solutions, *Talanta*, **2000**, 51, 145–149.
12. X. Xin-You, W. Zhi-Lin, M. Wei-Xin, L. Qin-Hui, N. Shi-Sheng, and X. Ji-De, Synthesis and Characterization of a New N-alkylated Azacrown Ligand and its Transition Metal Complexes, *Synt. React. Inorg. Metal-Org., and Nano-Metal Chem.*, **1997**, 27, 1071–1081.
13. K. Kimura, T. Maeda, and T. Shono, Extraction of Alkali Metal Picrates with Poly- and Bis(crown ether)s, *Talanta*, **1979**, 26, 945–949.
14. K. Kimura, T. Tsuchida, T. Maeda, and T. Shono, Properties of cis- and trans-bis(crown ether)s for Complexation and Extraction of Alkali Metal Picrates, *Talanta*, **1980**, 27, 801–805.
15. C. Hamamci, H. Hosgoren, and S. Erdogan, The Solvent Extraction of Alkali Metal Picrates with 4,13-*N,N'*-dibenzyl-4,13-diaza-18-crown-6, *Talanta*, **1998**, 47, 229–236.
16. B. Ziyadanogullari, G. Topal, S. Erdogan, C. Hamamci, and H. Hosgoren, Effect of Structural Modifications of Diaza-18-crown-6 on the Extractability and Selectivity of Univalent Metal Picrates, *Talanta*, **2001**, 53, 1083–1087.
17. A.P. Marchand, H.S. Chong, S. Alihodžić, W.H. Watson, and S.G. Bodige, Synthesis and Alkali Metal Picrate Extraction Capabilities of Novel, Cage-functionalized, Pyridine Containing Crown Ethers and Cryptands, *Tetrahedron*, **1999**, 55, 9687–9696.
18. U. Cakir and B. Cicek, Extraction Ability and Selectivity of Tetraaza-crown Ethers for Transition Metal Cations, *Trans. Met. Chem.*, **2004**, 29, 263–268.
19. Y. Takeda, K. Endo, S. Katsuta, and M. Ouichi, Extraction of Sodium and Potassium Picrates with 15-(2,5-dioxa-hexyl)-15-methyl-16-crown-5 (Iariat 16C5) into Various Organic Solvents. Elucidation of Fundamental Equilibria which Determine the Extraction Ability for Na<sup>+</sup> and K<sup>+</sup> and the Selectivity, *Talanta*, **2001**, 54, 575–584.
20. S. Katsuta, F. Tsuchiya, and Y. Takeda, Equilibrium Studies on Complexation in Water and Solvent Extraction of Zinc(II) and Cadmium(II) with Benzo-18-crown-6, *Talanta*, **2000**, 51, 637–644.
21. R.L. Bruening, R.M. Izatt, and J.S. Bradshaw, Understanding Cation-Binding Selectivity in Single-Solvent-Extraction, and Liquid Membrane Systems by Quantifying Thermodynamic Interactions, *Cation Binding by Macrocycles*, Y. Inoue and G.W. Gokel (eds.), Marcel Dekker, New York and Basel, **1990**, pp. 111–132.
22. M. Quochi, Y. Inoue, H. Sakamoto, M. Yamahira, and T. Hakushi, Crown Ethers of Low Symmetry. Spiro Crown Ethers and 16-crown-5 Derivatives, *J. Org. Chem.*, **1983**, 48, 3168–3173.
23. Y. Takeda, A. Kawarabayashi, K. Endo, T. Yahata, Y. Kudo, and S. Katsuta, Solvent Extraction of Alkali Metal (Li-Cs) Picrates with 18-crown-6 into Various Diluents. Elucidation of Fundamental Equilibria which Govern the Extraction-ability and -Selectivity, *Analytical Science*, **1998**, 14, 215.
24. U. Cakir, B. Cicek, Y.K. Yildiz, and M. Alkan, Solvent Effect upon Ion-pair Extraction of Different Sodium Dyes using Some Crown Ethers, *J. Incl. Phenom. and Macrocyclic. Chem.*, **1999**, 34, 153–165.
25. Y. Kudo, J. Usami, S. Katsuta, and Y. Takeda, Solvent Extraction of Permanganates (Na, K) by 18-crown-6 Ether from Water into 1,2-dichloroethane: Elucidation of an Extraction Equilibrium based on Component Equilibria, *Talanta*, **2003**, 59, 1213–1218.
26. H.I. Ugras, U. Cakir, A. Azizoglu, T. Kilic, and C. Erk, Experimental, Theoretical and Biological Activity Study on the Acyl-substituted Benzo-18-crown-6, Dibenzo-18-crown-6 and Dibenzo-24-crown-8, *J. Incl. Phenom. and Macrocyclic. Chem.*, **2006**, 55, 159–165.
27. Y. Takeda and H. Kato, The Solvent Extraction of Bivalent Metal Picrates by 15-crown-5, 18-crown-6, and Dibenzo-18-crown-6, *Bull. Chem. Soc. Jpn.*, **1979**, 52, 1027–1030.
28. L.F. Lindoy, *The Chemistry of Macrocyclic Ligand Complexes*, Cambridge University Press, **1989**, pp. 106–107.
29. U. Cakir, M. Ozer, M.A. Icen, H.I. Ugras, and M. Bulut, Synthesis of Some 3-phenyl Chromenone-crown Ethers and Equilibrium Studies on Complexation with Ion-pair Extraction of Sodium and Potassium Dyes, *Dyes and Pigments*, **2004**, 60, 177–185.
30. F. Karadeniz, Preparation of Some new Dibenzo and Dibebo-diaza crown ether precursors, PhD Thesis (in Turkish), Dicle University, Diyarbakir, Turkey; **2000**.
31. J.D. Lamb, R.M. Izatt, J.J. Christensen, and D.J. Eatough, Thermodynamics and Kinetics of Cation-Macrocyclic Interaction, *Coordination Chemistry of Macrocyclic Compounds*, G.A. Melson (ed.), Plenum Publishing Corp., New York, **1979**, pp. 145–217.
32. G.W. Gokel, *Crown Ethers & Cryptands*. The Royal Society of Chemistry, **1994**, 115.
33. V.V. Yakshin, A.T. Fedorova, and B.M. Laskorin, Extraction of Inorganic Metal Salts from Alkaline Solution by Crown Ethers, *Russian Chemical Bulletin*, **1986**, 35, 463–467 and references cited therein.
34. K.B. Yatsimirskii and Y.D. Lampeka, *Physicochemistry of Metal Complexes with Macrocyclic Ligands*, (in Russian), Naukova Dumka, Kiev, **1985**, pp. 256–260.
35. R.M. Clay, S. Corr, M. Micheloni, and P. Paoletti, Non-cyclic Reference Ligands for Tetraaza Macrocycles. Synthesis and Thermodynamic Properties of a Series of alpha, omega-di-N-methylated Tetraaza Ligands and their Copper(II) Complexes, *Inorg. Chem.*, **1985**, 24, 3330–3336.
36. V.K. Belsky and B.M. Bulychev, Structural-chemical Aspects of Complexation in Metal Halide-Macrocyclic Polyether Systems, *Russian Chemical Reviews*, **1999**, 68, 119–135.